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## Adsorption of Gases in Multimolecular Layers

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## Introduction

The adsorption isotherms of gases at temperatures not far removed from their condensation points show two regions for most adsorbents: at low pressures the isotherms are concave, at higher pressures convex toward the pressure axis. The higher pressure convex portion has been variously interpreted. By some it has been attributed to condensation in the capillaries of the adsorbent on the assumption that in capillaries of molecular dimensions condensation can occur at pressures far below the vapor pressure of the liquid. By others such isotherms are believed to indicate the formation of multimolecular adsorbed layers. DeBoer and Zwicker<sup>1</sup> explained the adsorption of non-polar molecules on ionic adsorbents by assuming that the uppermost layer of the adsorbent induces dipoles in the first layer of adsorbed molecules, which in turn induce dipoles in the next layer and so on until several layers are built up. The isotherm equation which they, and later Bradley,<sup>2</sup> derived on the basis of this polarization theory is practically the only quantitative expression that has been so far proposed to account for multimolecular adsorption. However, as we shall show in the first part of this paper, the polarization of the second layer of adsorbed gas by the first layer is already much too small to constitute the major portion of the binding energy between the two adsorbed layers, at least in those instances in which the gas molecules do not possess considerable permanent dipole moments.

It seems to us that the same forces that produce condensation are chiefly responsible for the binding energy of multimolecular adsorption. On this assumption, in the second part of this paper we shall carry out a derivation of the isotherm equation for multimolecular adsorption by a method that is a generalization of Langmuir's treatment of the unimolecular layer. In the third part of the paper we shall then apply the isotherm equation to a variety of experimental isotherms obtained by others and by us on a number of catalysts, catalyst supports and other adsorbents.

(1) DeBoer and Zwicker, *Z. physik. Chem.*, B3, 407 (1929).(2) Bradley, *J. Chem. Soc.*, 1467 (1936).

## I. The Polarization Theory of DeBoer and Zwicker

According to DeBoer and Zwicker, the induced dipole in the  $i$ th layer polarizes the  $i + 1$ st layer, thus giving rise to induced dipole moments and binding energies that decrease exponentially with the number of layers. If we call the dipole moment of a molecule in the  $i$ -th layer  $\mu_i$ , it follows that

$$\mu_i = c_1 C^i \quad (1)$$

where  $c_1$  and  $C$  are appropriate constants,  $C$  actually being equal<sup>3</sup> to  $\mu_i/\mu_{i-1}$ . The corresponding binding energy is proportional to the square of the dipole moment

$$\phi_i = c_2 C^{2i} \quad (2)$$

where  $c_2$  is another constant. The equilibrium pressure of the  $n$ th layer (top layer),  $p_n$ , according to Boltzmann's law varies exponentially with the binding energy of that layer and, if the only binding energy were that due to polarization, would be given by the equation

$$p_n = c_3 e^{-\phi_n/RT} \quad (3)$$

It follows, therefore, that

$$\ln \frac{p_n}{c_3} = -\frac{c_2}{RT} C^{2n} \quad (4)$$

which is identical with DeBoer and Zwicker's equation

$$\ln \frac{p_n}{K_1 p_0} = K_2 K_1^n \quad (4a)$$

if  $c_3$  be replaced by  $K_3 p_0$ ,  $-c_2/RT$  by  $K_2$ , and  $C^2$  by  $K_1$ .

One can substitute  $n = v/v_m$ , where  $v$  is the volume of gas adsorbed at pressure  $p_n$ , and  $v_m$  is the volume adsorbed in one complete unimolecular layer. DeBoer and Zwicker,<sup>1</sup> and subsequently

(3) According to DeBoer and Zwicker the  $\mu_i$  values for all layers, except the first and the top layer, satisfy the equations

$$\mu_i = k(\mu_{i-1} + \mu_{i+1}) \quad (1a)$$

Equation (1) is a solution of (1a) if

$$C = \frac{1 - \sqrt{1 - 4k^2}}{2k} \quad (1b)$$

DeBoer and Zwicker give the approximate expression

$$C = k/(1 - k^2) \quad (1c)$$

which for  $k \ll 1$  is a good approximation for (1b). It should be noted, however, that when  $k \ll 1$  only a few layers are usually adsorbed and, since equation (1a) is not valid for the top layer, in this case all of the equations are to be considered approximate. Bradley, using equation (1c), derived the values of 0.6075 and 0.615 for  $k$  for copper sulfate and aluminum sulfate, respectively, even though the upper limit of  $k$  according to (1b) is 0.5.

DeBoer<sup>4,5</sup> in several papers showed that various experimental adsorption isotherms could be fitted by equation (4a). However, they could not evaluate  $K_1$  because in all cases, except one, the surface, and therefore  $v_m$ , was not known. In the only case where the surface was known<sup>6</sup> the adsorption proved to be unimolecular in thickness, and thus the application of the equation would not have been justified.

Bradley<sup>3</sup> arrived at an equation identical to (4a) except that  $K_1$  is taken as unity. By applying it to his data for argon adsorption on copper sulfate and aluminum sulfate, and by estimating  $v_m$  from microscopic measurements of the diameters of the adsorbent particles, he evaluated  $K_1$ , and obtained  $k$  values of about 0.6. He concluded that the very strong polarization of adsorbed argon explained the relatively thick adsorption layers (at half of the saturation pressure more than 30 layers) that he believed he was obtaining. Emmett and Brunauer<sup>7</sup> have already pointed out reasons for believing that the surface areas of the samples used by Bradley were probably many times greater than he estimated, and that therefore his estimate of the thickness of his films was high by possibly a factor of 20 or so. It will now be shown that the ratio of the strength of the dipoles induced in the  $i$ th layer to that induced in the dipoles of the  $i-1$ st layer is of the order of 0.01 for argon rather than 0.99, a value that one obtains from Bradley's  $k = 0.615$  for aluminum sulfate. Accordingly the polarization of one layer of argon by the next lower layer is far too small to constitute the major portion of the binding energy between successive adsorbed layers.

The estimation of the magnitude of  $C$ , the ratio of the strength of the induced dipoles in two successive layers, can be carried out in the following manner. The field of a dipole  $\mu_1$  at a distance  $r$  is proportional to  $\mu_1/r^3$ , and the dipole,  $\mu_2$ , induced in a molecule of polarizability  $\alpha$  at that distance is proportional to  $\mu_1\alpha/r^3$ . The ratio  $\mu_2/\mu_1$  is therefore proportional to the dimensionless number  $\alpha/r^3$ , and the ratio of the binding energies in two successive layers to  $\alpha^2/r^6$ .

The polarizability of a gas molecule,  $\alpha$  is given by the equation

$$2\pi\alpha = (n-1)v_g, \quad (5)$$

where  $n$  is the index of refraction extrapolated to

(4) DeBoer, *Z. physik. Chem.*, B13, 134 (1931).

(5) DeBoer, *ibid.*, B14, 149 (1931).

(6) DeBoer, *ibid.*, B17, 161 (1932).

(7) Emmett and Brunauer, *This Journal*, 59, 1663 (1937).

infinite wave length, and  $v_g$  is the gram molecular volume of the gas divided by Avogadro's number.

We shall assume, to start with, that the separation of the argon atoms in the adsorbed state is about the same as in the solid state. For a face-centered cubic lattice, such as that of solid argon, the distance  $r$  between the nearest neighbors is given by the equation

$$r^3 = \sqrt{2}v_g \quad (6)$$

where  $v_g$  is the molecular volume of the solid divided by Avogadro's number. It follows from (5) and (6) that

$$\frac{\alpha}{r^3} = \frac{n-1}{2^{1/2}} \frac{v_g}{v_g} \quad (7)$$

For argon gas at 0° and 760 mm. pressure,  $n-1 = 278 \times 10^{-48}$  and by using the density of solid argon at 40°K.<sup>9</sup> one obtains

$$\alpha/r^3 = 0.029 \quad (8)$$

If we assume that the separation of the argon atoms in the adsorbed state is the same as in the liquid state,  $\alpha/r^3$  becomes even smaller.

The ratio of the induced dipoles in two successive layers is given by the equation

$$(\mu_{i+1})/\mu_i = C = d(\alpha/r^3) \quad (9)$$

where  $d$  is a constant dependent upon the geometrical structure of the adsorbed layers and the relative orientation of the induced dipoles. If the adsorbed argon atoms build up in a close-packing of spheres and the dipoles in one layer are all oriented in the same direction and perpendicular to the surface, then the value calculated for  $d$  becomes  $-0.35$ .<sup>10</sup> The minus sign

(8) "International Critical Tables," Vol. VII, p. 11.

(9) *Ibid.*, Vol. I, p. 103.

(10) The  $x$  component of an electric field produced at a distance  $\rho$  by a dipole  $\mu$  pointing in the  $x$  direction is  $\mu \left\{ \frac{3(x_1 - x_2)^2}{\rho^5} - \frac{1}{\rho^3} \right\}$

where  $x_1$  and  $x_2$  are  $x$  coordinates of the dipole and the point at which the field is calculated. We take the  $x$  direction perpendicular to the surface, and we denote by  $r$ , as before, the distance between the nearest neighbors. Then  $x_1 - x_2$  for atoms in the same layer is zero, and for atoms in successive layers is  $\sqrt{2/3}r$  for close-packing of spheres. Then the field produced in the center of an atom in the  $i$ th layer by all the other atoms in the same layer is  $-\mu_i \Sigma (1/\rho^3)$ , where the summation has to be extended over all the other atoms of the layer. The field produced in the center of this same atom by all the atoms in the  $i-1$ st and  $i+1$ st layer is  $(\mu_{i-1} + \mu_{i+1}) \Sigma \left( \frac{2r^3}{\rho^5} - \frac{1}{\rho^3} \right)$ . The numerical evaluation of the infinite sums yields the results  $-\mu_i(11.1/r^3)$  and  $(\mu_{i-1} + \mu_{i+1})(8.357 - 8.823/r^3)$ . The dipole  $\mu_i$  induced in the atom by the sum of these forces is

$$\mu_i = \frac{\alpha}{r^3} \{ -11.1\mu_i - 0.466(\mu_{i-1} + \mu_{i+1}) \}$$

giving for  $\alpha/r^3 = 0.029$  the result

$$\mu_i = -0.35 \frac{\alpha}{r^3} (\mu_{i-1} + \mu_{i+1})$$

Comparison with equation (1a) in the footnote to page 2 shows that  $k = 0.35 \alpha/r^3$ , and since  $k \ll 1$ , therefore  $k$  is approximately equal to  $C$ .

signifies that the dipoles in successive layers point alternately toward the surface and away from the surface. From (8) and (9) we obtain  $C = -0.01$  and therefore  $K_1$  (of equation 4a), or  $C^2$  (of equation 4) equals about  $1 \times 10^{-4}$ . Hence the binding energy that can be attributed to polarization is negligibly small already in the second layer.

In the calculation of  $d$  it was assumed that the dipoles can be localized in the centers of the atoms, and are induced by forces acting at the centers of the atoms. Furthermore, the calculation was made only for the case in which the dipoles in a given layer all point in the same direction and are perpendicular to the surface. Though it is realized that for slightly different assumptions and for different arrangements and orientations of the dipoles the value of  $d$  will differ from the above, it seems certain that for gases for which  $\alpha/r^3$  is as small as for argon, the portion of the binding energy due to polarization forces operating between the various layers of adsorbed gas must be very small. For molecules with larger polarizability  $\alpha/r^3$  will, of course, be larger than for argon. DeBoer chose iodine for his experiments because of its larger polarizability. Even in this case, however, since  $\alpha/r^3$  is about 0.1 it is unlikely that the energy of binding due to polarization will constitute an appreciable portion of the binding energy of the second layer of adsorbed iodine. On the other hand, if the adsorbed gas has a large permanent dipole it is possible that many layers may be successively polarized by the mechanism of DeBoer and Zwicker. This case has been treated by Bradley.<sup>11</sup>

It may be well at this point to call attention to the fact that equation (4a) in its logarithmic form and with  $K_s$  equal to unity has been used frequently to present adsorption data. Thus a plot of  $\log \log p/p_0$  against the amount adsorbed has often been found to be linear over a considerable range of  $p/p_0$  values. In view of our conclusions relative to the polarization theory it seems that such representations are to be regarded, for the present, as empirical though interesting relationships.

## II. Generalization of Langmuir's Theory to Multimolecular Adsorption

With the help of a few simplifying assumptions it is possible to carry out an isotherm derivation

for multimolecular layers that is similar to Langmuir's derivation for unimolecular layers. The equations obtained appear not only to represent the general shape of the actual isotherms, but to yield reasonable values for the average heat of adsorption in the first layer and for the volume of gas required to form a unimolecular layer on the adsorbents.

In carrying out this derivation we shall let  $s_0, s_1, s_2, \dots, s_i, \dots$  represent the surface area that is covered by only 0, 1, 2,  $\dots, i, \dots$  layers of adsorbed molecules. Since at equilibrium  $s_0$  must remain constant the rate of condensation on the bare surface is equal to the rate of evaporation from the first layer

$$a_1 p s_0 = b_1 s_1 e^{-E_1/RT} \quad (10)$$

where  $p$  is the pressure,  $E_1$  is the heat of adsorption of the first layer, and  $a_1$  and  $b_1$  are constants. This is essentially Langmuir's equation for unimolecular adsorption, and involves the assumption that  $a_1, b_1$ , and  $E_1$  are independent of the number of adsorbed molecules already present in the first layer.

At equilibrium  $s_1$  must also remain constant,  $s_1$  can change in four different ways: by condensation on the bare surface, by evaporation from the first layer, by condensation on the first layer, and by evaporation from the second layer. We thus obtain

$$a_2 p s_1 + b_1 s_1 e^{-E_1/RT} = b_2 s_2 e^{-E_2/RT} + a_1 p s_0 \quad (11a)$$

where the constants  $a_2, b_2$ , and  $E_2$  are similarly defined to  $a_1, b_1$  and  $E_1$ . From (10) and (11a) follows

$$a_2 p s_1 = b_2 s_2 e^{-E_2/RT} \quad (11)$$

the rate of condensation on top of the first layer is equal to the rate of evaporation from the second layer.<sup>12</sup> Extending the same argument to the second and consecutive layers we obtain

$$\begin{aligned} a_3 p s_2 &= b_3 s_3 e^{-E_3/RT} \\ &\vdots \\ a_i p s_{i-1} &= b_i s_i e^{-E_i/RT} \end{aligned} \quad (12)$$

The total surface area of the catalyst is given by

$$A = \sum_{i=0}^{\infty} s_i \quad (13)$$

(12) Equation (11) could have been arrived at immediately by applying the principle of microscopic reversibility, because the number of evaporation processes by which  $s_1$  decreases and  $s_1$  increases must be equal to the number of condensation processes by which  $s_1$  increases and  $s_1$  decreases. It follows also from the same principle that every other process that can occur (such as, for example, the sliding over of a molecule from one layer into another), will be balanced by a reverse process of equal frequency. Thus the equilibrium, expressed in (11), will not be influenced by such further processes.

(11) Bradley, *J. Chem. Soc.*, 1799 (1936).

and the total volume adsorbed is

$$v = v_0 \sum_{i=0}^{\infty} s_i \quad (14)$$

where  $v_0$  is the volume of gas adsorbed on one square centimeter of the adsorbent surface when it is covered with a complete unimolecular layer of adsorbed gas. It follows that

$$\frac{v}{Av_0} = \frac{v}{v_m} = \frac{\sum_{i=0}^{\infty} s_i}{\sum_{i=0}^{\infty} s_i} \quad (15)$$

where  $v_m$  is the volume of gas adsorbed when the entire adsorbent surface is covered with a complete unimolecular layer.

The summation indicated in equation (15) can be carried out if we make the simplifying assumptions that

$$E_1 = E_2 = \dots E_i = E_L \quad (16)$$

where  $E_L$  is the heat of liquefaction, and

$$\frac{b_1}{a_1} = \frac{b_2}{a_2} = \dots \frac{b_i}{a_i} = g \quad (17)$$

$g$  being an appropriate constant. This is equivalent to saying that the evaporation-condensation properties of the molecules in the second and higher adsorbed layers are the same as those of the liquid state. We can express now  $s_1, s_2, s_3, \dots s_i$  in terms of  $s_0$ .

$$s_1 = ys_0, \text{ where } y = (a_1/b_1)pe^{E_1/RT} \quad (18)$$

$$s_2 = xs_1, \text{ where } x = (p/g)e^{E_1/RT} \quad (19)$$

$$s_3 = xs_2 = x^2s_1 \quad (20)$$

$$s_i = xs_{i-1} = x^{i-1}s_1 = yx^{i-1}s_0 = cx^i s_0 \quad (21)$$

$$\text{where } c = \frac{y}{x} = \frac{a_1g}{b_1} e^{E_1 - E_L/RT} \quad (22)$$

Substituting into equation (15) we obtain

$$\frac{v}{v_m} = \frac{cs_0 \sum_{i=1}^{\infty} ix^i}{s_0 \left\{ 1 + c \sum_{i=1}^{\infty} x^i \right\}} \quad (23)$$

The summation represented in the denominator is merely the sum of an infinite geometric progression

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1-x} \quad (24)$$

Concerning the summation in the numerator we may note that

$$\sum_{i=1}^{\infty} ix^i = x \frac{d}{dx} \sum_{i=1}^{\infty} x^i = \frac{x}{(1-x)^2} \quad (25)$$

It follows therefore that

$$\frac{v}{v_m} = \frac{cx}{(1-x)(1-x+cx)} \quad (26)$$

If we deal with adsorption on a free surface, then at the saturation pressure of the gas,  $p_0$ , an infinite number of layers can build up on the adsorb-

ent. To make  $v = \infty$ , when  $p = p_0$ ,  $x$  must be equal to unity. Thus from (19)

$$(p_0/g)e^{E_L/RT} = 1, \text{ and} \\ x = p/p_0 \quad (27)$$

Substituting into (26) we obtain the isotherm equation

$$v = \frac{v_m c p}{(p_0 - p) \{ 1 + (c-1)(p/p_0) \}} \quad (28)$$

The following considerations show that equation (28) gives, indeed, an S-shaped isotherm. The constant  $c$ , as a rule, will be large compared to unity, and therefore the isotherm will consist of two regions. The low pressure region will be concave to the pressure axis, and for  $p \ll p_0$  equation (28) reduces to

$$v = \left( \frac{v_m c}{p_0} p \right) / \left( 1 + \frac{c}{p_0} p \right) \quad (29)$$

which is a special form of the Langmuir equation. At higher pressures, as  $p$  approaches  $p_0$ ,  $v$  becomes large, and the curve becomes convex to the pressure axis.

For the purpose of testing, equation (28) can be put in the form

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \frac{p}{p_0} \quad (A)$$

Equation (A) is in a convenient form, since a plot of  $p/v(p_0 - p)$  against  $p/p_0$  should give a straight line, whose intercept is  $1/v_m c$  and whose slope is  $(c-1)/v_m c$ . Thus from the slope and intercept the two constants  $v_m$  and  $c$  can be evaluated, the former being the volume of gas required to form a complete unimolecular adsorbed layer, the latter, as we shall see later, being approximately equal to  $e^{E_1 - E_L/RT}$ . The application of this equation to experimental data will be given in the next section.

If the thickness of the adsorbed layers cannot exceed some finite number  $n$ , then the summation of the two series in equation (23) is to be carried to  $n$  terms only, and not to infinity. Instead of equation (A) one obtains then

$$v = \frac{v_m c x}{(1-x)} \left\{ \frac{1 - (n+1)x^n + nx^{n+1}}{1 + (c-1)x - cx^{n+1}} \right\} \quad (B)$$

where  $x = p/p_0$ , as before, and the constants  $v_m$  and  $c$  have also the same meaning as before. A rather plausible interpretation of the constant  $n$  is that the width of the pores, cracks and capillaries of the adsorbent sets a limit to the maximum number of layers that can be adsorbed even at saturation pressure. It is conceivable that other causes than the diameters of the capillaries can put such a limitation to the maximum

number of layers that can build up. However, even if this be the case, the result, equation (B), may still remain valid.

Equation (B) has two important limiting cases, both of which we shall make use of later. When  $n = 1$ , it reduces to the Langmuir type equation (29) and when  $n = \infty$  (free surface), it reduces to equation (A). Furthermore, it should be noted that when  $x$  has a small value, and  $n$  is as large as 4 or 5, equation (A) becomes a very good approximation to (B). To use equation (B), therefore, one should plot the experimental isotherm in the low pressure region according to the linear form of (A), evaluate  $c$  and  $v_m$  from the slope and intercept of the straight line, then using these values in equation (B) solve for the best average value of  $n$ . We shall apply this equation also to experimental data in the next section.<sup>13</sup>

The formation of multimolecular layers on an adsorbent below the saturation pressure, according to the present view, is analogous in many respects to the formation of multimolecular clusters in a non-ideal gas. There is, however, an important difference. In the gas the number of multimolecular clusters is negligible compared to the number of single molecules (except in the

(18) For the sake of completeness we include here two other equations.

1. If we assume that  $E_2$ , the heat of adsorption in the second layer, is still somewhat larger than the heat of liquefaction, ( $E_2 = E_1 = \dots = E_L$ ); and further assume that the packing in the first layer is different from the packing in the higher layers, then the adsorption isotherm equation for a free surface becomes

$$v = \frac{v_m c x}{(1-x)} \left\{ \frac{\delta + (b-\delta)(2x-x^2)}{1 + (c-1)x + (b-1)cx^2} \right\} \quad (C)$$

where  $b = e^{E_2 - E_L/RT}$ , and  $\delta = v_m(i)/v_m$ , where  $v_m(i)$  is the volume of gas adsorbed in the first layer when it is completely covered, and  $v_m$  is the volume adsorbed in any higher complete layer. All the other terms in the equation have the same meaning as in (A) and (B). It is to be expected that  $\delta$  is not very different from unity. Setting  $\delta = 1$ , and  $b > 1$ , equation (C) gives a faster rise in  $v$  with increasing pressure than (A) does. Example of this has been found in the adsorption of butane on silica gel (see third part of this paper).

2. In the derivation of equation (B) we assumed that  $n$  was the maximum number of layers that can build up on any part of the adsorbing surface. As long as the capillaries of an adsorbent are fairly uniform in diameter, equation (B) can describe the entire course of the isotherm with a fair degree of accuracy. If, on the other hand, the size of the pores in an adsorbent varies considerably from the average, the experimental points will fall below the theoretical curve calculated with the help of equation (B) at lower pressures, and above the curve at higher pressures. The equation which takes care of the varying size of the capillaries is

$$v = \frac{v_m c x}{(1-x)} \sum_{n=1}^{\infty} \beta_n \left\{ \frac{1 - (n+1)x^n + nx^{n+1}}{1 + (c-1)x - cx^{n+1}} \right\} \quad (D)$$

where  $v_m$  is the volume of gas adsorbed in the complete first layer and  $\beta_1, \beta_2, \dots, \beta_i$  are the fractions of the total surface on which a maximum of 1, 2,  $\dots, i$  layers can build up. Because of the large number of constants in equation (D), its practical use is difficult. However, fortunately, equation (B) is usually a good enough approximation to describe the actual experimental isotherms,

neighborhood of the critical point), whereas on a surface multimolecular layers will form far below the saturation pressure. This difference is to be accounted for on the basis of surface tension considerations. In the gas phase the large free surface energy of small clusters makes their formation improbable. On the other hand, in adsorption the "liquid surface" is practically complete after the first layer has been adsorbed, so that during the formation of successive layers hardly any surface tension has to be overcome.

### III. Application of the Theory of Multimolecular Adsorption to Experimental Data

A. S-Shaped Isotherms.—In several recent papers<sup>7,14,15</sup> we have published low temperature van der Waals adsorption isotherms for some or all of the gases nitrogen, oxygen, argon, carbon monoxide, carbon dioxide, sulfur dioxide, and butane on some 30 samples of catalysts, catalyst supports, and miscellaneous materials, including various promoted and unpromoted iron synthetic ammonia catalysts, metallic copper catalysts, pumice, nickel oxide supported on pumice, nickel on pumice, copper sulfate pentahydrate, anhydrous copper sulfate, potassium chloride, crystalline chromium oxide, chromium oxide gel, glaucosil, silica gel, soils and soil colloids, dried powdered bacteria, Darco (decolorizing carbon), and charcoal. On all of these substances, except charcoal, typical S-shaped isotherms have been obtained, the low pressure portion of the isotherm being concave to the pressure axis, the higher pressure region convex to the pressure axis, and the intermediate region approximately linear with respect to pressure. To these S-shaped isotherms equations (A) and (B) have been applied. Typical plots of equation (A) are shown in Fig. 1 for the adsorption of nitrogen at 90.1°K. on a variety of adsorbents, and in Fig. 2 for the adsorption of various gases on silica gel. Between relative pressures ( $p/p_0$ ) of 0.05 and 0.35 the plots are closely linear. From them the values of  $v_m$  and  $c$  can be evaluated as explained in the previous section. From  $c$  one can obtain an approximate value for  $E_1 - E_L$ .<sup>16</sup>

(14) Emmett, Brunauer and Love, *Soil Science*, to be published.

(15) Brunauer and Emmett, *This Journal*, 59, 2383 (1937).

(16) According to equations (17) and (22)

$$c = \frac{a_1 b_2}{b_1 a_2} e^{E_1 - E_L/RT}$$

From the nature of the constants  $a_1, a_2, b_1$  and  $b_2$  it is evident that  $a_1 b_2 / b_1 a_2$  will not differ much from unity, and therefore  $E_1 - E_L$  will be  $2.303RT \log c$ .

TABLE I  
VALUES OF CONSTANTS FOR ADSORPTION OF NITROGEN  
AT 90.1°K. ON VARIOUS ADSORBENTS

Substance	Curve in Fig. 1	$v_m$ in cc. per g.	Point B in cc. per g.	$E_1 - E_L$ in cal. per mole
Unpromoted Fe catalyst 973I		0.13	0.12	794
Unpromoted Fe catalyst 973II	1	0.29	0.27	774
Fe-Al <sub>2</sub> O <sub>3</sub> catalyst 954		2.86	2.78	894
Fe-Al <sub>2</sub> O <sub>3</sub> catalyst 424	2	2.23	2.09	774
Fe-Al <sub>2</sub> O <sub>3</sub> -K <sub>2</sub> O catalyst 931		0.81	0.76	911
Fe-Al <sub>2</sub> O <sub>3</sub> -K <sub>2</sub> O catalyst 958	3	.56	.55	854
Fe-K <sub>2</sub> O catalyst 930		.14	.12	772
Fused Cu catalyst	4	.05	.05	776
Commercial Cu catalyst		.09	.10	834
Cr <sub>2</sub> O <sub>3</sub> gel	5	53.3	50.5	738
Cr <sub>2</sub> O <sub>3</sub> glowed		6.09	6.14	835
Silica gel	6	116.2	127.0	794

Table I gives the constants  $v_m$  and  $E_1 - E_L$  for the six adsorption isotherms represented in Fig. 1 as well as for six other isotherms not shown in the figure. The constants  $v_m$  in the table are given for one gram of the adsorbent rather than for the entire sample.

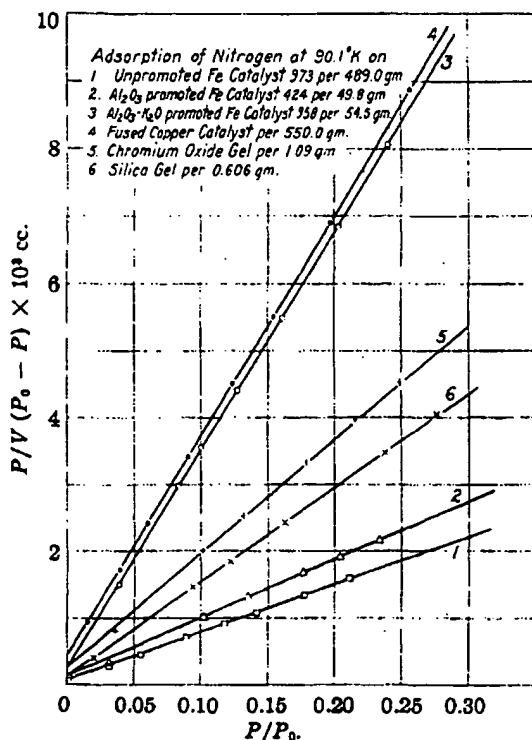


Fig. 1.

In several previous publications Emmett and Brunauer concluded that the beginning of the approximately linear portion of the experimentally determined low temperature adsorption isotherms (point B in Fig. 3 for example), corresponds to the covering of the surface of the adsorbent by

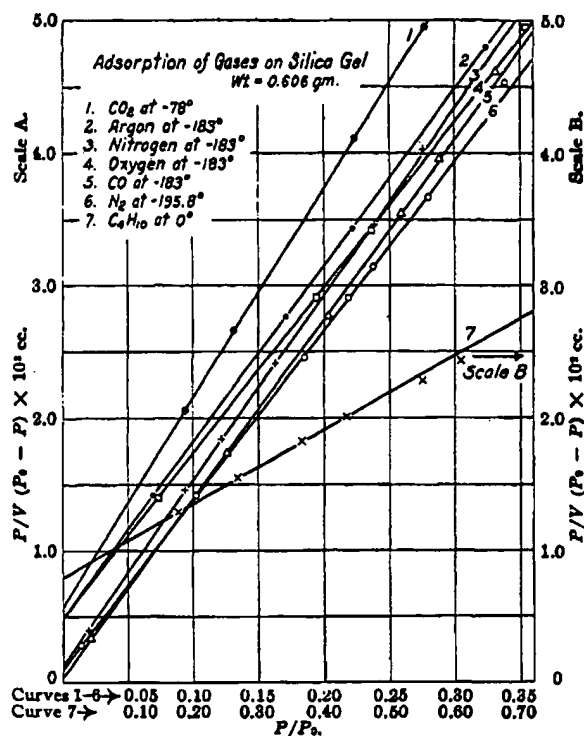


Fig. 2.

a complete unimolecular layer of adsorbed gas. Since the constant  $v_m$ , evaluated from the straight line plots of equation (A), is also the volume of gas corresponding to a unimolecular layer, values

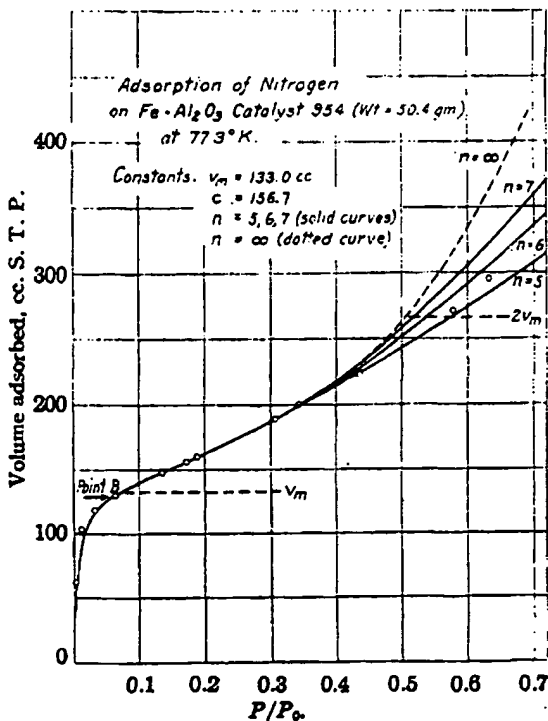


Fig. 3.

of  $v_m$  and of the volume of gas adsorbed at point B on the various isotherms should in general agree closely with each other. Columns 3 and 4 of Table I give a comparison between the  $v_m$  values and the adsorption volumes corresponding to point B for twelve isotherms. It is evident that the agreement is very satisfactory, the two seldom differing by as much as 10%.

The last column of Table I reveals an interesting constancy in the value of the heat of adsorption in the first layer for different adsorbents. For nitrogen  $E_1 - E_L$  is uniformly  $840 \pm 70$  cal. Since  $E_L$  is about 1330 cal.,  $E_1$  is therefore  $2170 \pm 70$  cal. for nitrogen on all twelve adsorbents. At first thought this uniformity may seem rather surprising. It must be remembered, however, that  $E_1$  is by definition an *average* heat of adsorption for the first layer. Furthermore, as is evident from Figs. 1 and 2, for  $p/p_0$  values smaller than about 0.05 the experimental points do not fall on the linear plot, in other words, equation (A) breaks down for the most active points on the surface. (The reason for this is probably that the assumption that  $E_1$  is independent from the amount of gas already adsorbed in the first layer, becomes untenable for the most active part of the surface.) Hence  $E_1$ , as obtained from the linear plot, must be regarded as the average heat of adsorption for the less active part of the adsorbing surface.

It is interesting to note that, as shown in Table II, the value of  $E_1 - E_L$  is approximately constant for a given gas regardless of the chemical nature of the adsorbent. Thus on such different substances as a singly promoted iron synthetic ammonia catalyst and silica gel, the values of  $E_1 - E_L$  are for nitrogen  $840 \pm 50$  cal., for argon  $650 \pm 55$  cal., for carbon dioxide  $1460 \pm 120$  cal., and for butane  $1900 \pm 30$  cal. Furthermore, as is evident from Figs. 1 and 2, the values of the intercepts,  $1/v_m c$ , are small in all cases. The consequence of these facts is that a single adsorption point for any gas for which an approximate value of  $E_1 - E_L$  is known will enable one to fix  $v_m$  within comparatively narrow limits for any finely divided solid known to be characterized by S-shaped isotherms. For example if the highest pressure point of Curve 4, Fig. 1, were connected by a straight line to the origin, the slope of the resulting line (and therefore the value of  $v_m$ ) would differ from that for the curve as now drawn by no more than 3%. Indeed, the slope of a

straight line connecting the 760-mm. adsorption point for nitrogen at  $-183^\circ$  with the origin on a plot of equation (A) such as is shown in Figs. 1 and 2, is equal to  $1/v_m$  with an error of no more than 5% on all solid adsorbents with which we have worked that gave S-shaped isotherms (enumerated at the beginning of this section). This is the same as saying that  $v_m = v(1 - p/p_0)$ , so that, for example,  $v_m$  is  $2/3$  of the volume of gas adsorbed when  $p/p_0 = 1/3$ .

TABLE II

Substance	VALUES FOR DIFFERENT GASES			
	$N_2$ at $-183^\circ$	A at $-183^\circ$	$CO_2$ at $-78^\circ$	$C_4H_{10}$ at $0^\circ$
$Al_2O_3$ promoted Fe catalyst 954	894	704	1580	1870
Silica gel	794	594	1335	1930

After the value of  $v_m$  is obtained from the isotherm, multiplication of the number of molecules required to form a unimolecular layer by the average area occupied by each molecule on the surface gives the absolute value of the surface area of the adsorbent. In Table III the surface area in square meters per gram has been calculated from the isotherms of different gases adsorbed on silica gel, using the  $v_m$  values listed in Column 4, and the cross sectional areas of the adsorbed molecules calculated from both the density of the solidified gas and of the liquefied gas.<sup>17</sup> It is evident from Columns 5 and 6 that the areas calculated from one gas agree approximately with those calculated from another gas. On the basis of solid-like packing the average surface area obtained from the seven isotherms is 440 square meters per gram of silica gel, and the maximum deviation from the average is 15%; on the basis of liquid-like packing the average surface is 500 square meters per gram, and the maximum deviation is 10%. In Table III, Column 7, is listed the value of adsorption at Point B on the seven adsorption isotherms. It will be seen that for six isotherms the agreement between  $v_m$  and the volume at Point B is very good, but for butane the former is twice as large as the latter. For some as yet unknown reason the empirical choosing of Point B as corresponding to a unimolecular layer apparently gives erroneous results for butane on silica gel. The  $v_m$  value, on the other hand, as is evident from Table III, yields a surface area for the silica gel

(17) For a table of these cross sectional molecular areas and details of calculation see Emmett and Brunauer, *THIS JOURNAL*, 59, 1532 (1937).

that is consistent with that calculated from the other gases.

TABLE III  
VALUE OF CONSTANTS FOR ADSORPTION ISOTHERMS ON  
SILICA GEL

Gas	Temp. °C.	Curve in Fig. 2	$v_m$ , cc./g.	Surface in sq. m./g. Solid pack- ing Liquid packing	Point B cc./g.	$E_1 - E_L$ cal. per mole
N <sub>2</sub>	-195.8	6	127.9	477 580	135.3	719
N <sub>2</sub>	-183	3	116.2	434 534	127.0	794
A	-183	2	119.3	413 464	122.0	594
O <sub>2</sub>	-183	4	125.1	410 477	132.0	586
CO	-183	5	121.2	449 550	132.0	973
CO <sub>2</sub>	-78	1	99.0	378 455	102.3	1335
C <sub>4</sub> H <sub>10</sub>	0	7	58.2	504 504	28.1	1930

At relative pressures in excess of about 0.35 to 0.50 the plot of experimental data according to equation (A) deviates with increasing pressures more and more strongly from the straight line. The points deviate in the direction of there being too little adsorption at a given  $p/p_0$  value to conform to equation (A). It becomes therefore necessary to use instead equation (B). As already explained one can first evaluate  $c$  and  $v_m$  by applying equation (A) up to  $p/p_0 = 0.35$ , and can then proceed to use these values in equation (B) to obtain by the method of trial and error the value of  $n$  that gives best agreement with the experimental points. In certain instances, as in

Fig. 3, a value of  $n$  ( $n = 5$ ) fits the data well up to a certain relative pressure ( $p/p_0 = 0.58$ ), but at higher relative pressures higher values of  $n$  give the better fit ( $n = 7$  at  $p/p_0 = 0.72$ ). If one takes an average value of  $n = 6$ , the theoretical curve will be in error to the extent of +5% at  $x = 0.58$ , and -7% at  $x = 0.72$ . On the basis of the capillary interpretation this means that the iron catalyst in question has pores of considerably varying diameters. On the other hand, an adsorption isotherm of oxygen at -183° on the adsorbent Granular Darco G (activated carbon), could be fitted with a value of  $n = 2.2$  from  $x = 0.02$  to 0.93, and none of the experimental points were off the curve as much as 4%, indicating a rather uniform pore size in this adsorbent.

For substances giving S-shaped isotherms  $n$  values have been found to range from the low value of 2 for Darco decolorizing carbons to values of 8 or 9 for some silica gel samples. It is interesting to note in this connection that for the adsorption of butane on silica gel, as shown in Curve 7, Fig. 2, the higher pressure deviations from the linear plot are in the direction of too much adsorption rather than too little adsorption. One would expect just such deviation if the heat of adsorption in the second layer were still appreciably greater than the heat of liquefaction rather than equal to it, as was assumed in the derivations of equations (A) and (B).<sup>18</sup>

In order to be able to calculate from one isotherm another at a different temperature, one must examine how  $c$ ,  $v_m$  and  $n$  change with temperature. The dependence of  $c$  on temperature is exponential since  $c$  is approximately equal to  $e^{(E_1 - E_L)/RT}$ , and  $E_1 - E_L$  changes only slightly with temperature.  $v_m$  would be expected to vary with temperature owing to the thermal expansion of the adsorbed layer as the temperature increases. As a first approximation one may assume that  $v_m$  changes with temperature as  $d_L^{2/3}$ , where  $d_L$  is the density of the liquefied gas. By the same argument  $n$  should vary approximately as  $d_L^{1/3}$ , which is, indeed, a very slight variation. It was found empirically that the variation in  $n$  is actually negligible. With these assumptions the adsorption isotherms for singly promoted iron catalyst 954 at -195.8° have been calculated from the -183° isotherms for nitrogen and argon. The results are shown in Fig. 4. The agreement between the calculated curves and the experimental points appears to be quite satisfactory.

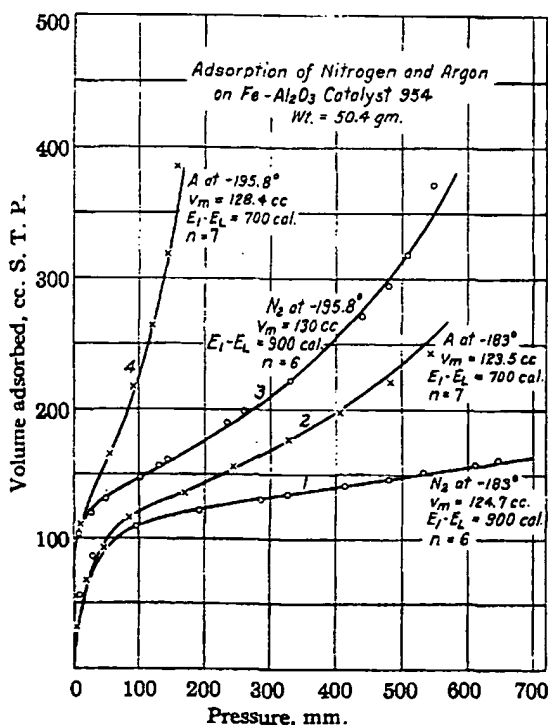


Fig. 4.



Unfortunately one cannot always safely assume that  $v_m$  changes with temperature as  $d_L^{2/3}$ . The change in  $v_m$  sometimes may be considerably greater, and sometimes less. An example of the former is afforded by the adsorption isotherms of McGavack and Patrick<sup>18</sup> for sulfur dioxide on silica gel at temperatures between  $-80$  and  $40^\circ$ . In Table IV, Column 2, the  $v_m$  values are listed for the six isotherms. It will be noted that  $v_m$  for  $-80^\circ$  is 1.43 times as great as for  $40^\circ$ , whereas it should only be 1.15 times as great if  $v_m$  would have changed as  $d_L^{2/3}$ . It is also to be noted that in these isotherms the  $E_1 - E_L$  value decreases markedly with decreasing temperature.

TABLE IV  
VALUE OF CONSTANTS OF ADSORPTION OF SULFUR DIOXIDE  
ON SILICA GEL (MCGAVACK AND PATRICK)

Temp. ° C.	$v_m$ , cc./g.	$d_L$ , g./cc.	$E_1 - E_L$ , cal./mole	$E_L$ , cal./mole	$E_1$ , cal./mole
40	91.6	1.327	1789	4940	6730
30	96.6	1.356	1750	5190	6940
0	105.8	1.435	1705	5840	7540
-34.4	118.6	1.522	1587		
-54	129.2	1.573	1458		
-80	131.0	1.642	1364		

$n = 3.5$  for all six isotherms.

The experimental data of Bradley<sup>2</sup> for argon on anhydrous copper sulfate, as well as our own for this system,<sup>19</sup> also can be represented satisfactorily by equation (B).  $E_1 - E_L$  was found to be 745 cal. for Bradley's isotherms, 777 for our own,  $n$  was about 5 for both cases. The surface of our copper sulfate sample was larger;  $v_m$  for Bradley's isotherms was  $6.4 \times 10^{-3}$  mole of argon per mole of copper sulfate, our value of  $v_m$  was  $10.8 \times 10^{-3}$  mole per mole. It should be noted that the value of  $v_m$  for Bradley's argon isotherm on copper sulfate which we consider to be a unimolecular layer was interpreted by Bradley as being about 18.5 layers.

Recently Palmer and Clark<sup>19</sup> published adsorption isotherms of acetone, benzene, and other organic vapors on samples of vitreous silica whose total surface area had been measured by comparing the initial rate of solution in hydrofluoric acid of the powdered sample with the rate of solution of a sample whose area was known. If one plots the adsorption isotherms of acetone on vitreous silica according to equation (A) one obtains a very good straight line whose slope cor-

responds to a  $v_m$  value of 50.6 micromoles of acetone on a 14.67 g. sample of vitreous silica. The specific surface of this same sample was 4690 sq. cm. according to Palmer and Clark's measurements of the rate of solution in hydrofluoric acid. If one uses for the area occupied by one acetone molecule on the surface the value  $26.9\text{\AA}^2$  (which is obtained from the density of liquid acetone at  $25^\circ$ ), one obtains from the above  $v_m$  value a specific surface of 5640 sq. cm., which is about 20% larger than Palmer and Clark's value. If on the other hand one uses for the area occupied by an acetone molecule the value  $20.5\text{\AA}^2$ , obtained by N. K. Adam for close-packed films on water of long-chain compounds terminating in the CO-CH<sub>3</sub> group, one obtains for the specific surface 4290 sq. cm., which is about 8% smaller than the value of Palmer and Clark. These data suffice to show that the agreement is very good, and in our opinion is a weighty confirmation of the method that they used for measuring the surface of vitreous silica.

#### B. Adsorption Isotherms on Charcoal

On charcoal, in contrast to all other adsorbents thus far tried by us, no S-shaped isotherms were obtained. The slopes of the isotherms on charcoal decrease continually as the pressure increases, and in the neighborhood of saturation become practically zero. Such isotherms can be fitted with equation (B) if  $n = 1$ . If we interpret the limitation in the number of layers that can build up on a surface as due to capillaries in the adsorbent, then we must conclude that the pores or capillaries in charcoal are exceedingly narrow, not more than one or two molecular diameters in thickness.<sup>20</sup>

If  $n = 1$ , equation (B) reduces to the form

$$p/v = p_0/cv_m + p/v_m \quad (E)$$

which is clearly a special form of the Langmuir equation. In Fig. 5 six isotherms on charcoal are plotted according to equation (E),  $p/v$  being taken as ordinate and  $p$  as abscissa. It will be noted that the plots are accurately linear from  $p/p_0 = 0.1$  clear up to the saturation pressure. Table V shows the constants  $v_m$  evaluated from

(20) Perhaps it is not immediately obvious that the evaporation-condensation equilibria expressed in equations (10), (11), and (12) can be applied to cases where the width of the capillaries is not more than one, two or a few molecular diameters. The principle of microscopic reversibility, however, shows that these equations remain valid even though the processes of direct condensation from or evaporation into the gas-phase play only a small part in the total equilibrium. The effect of these narrow capillaries will be merely to slow down the establishment of equilibrium.

(18) McGavack and Patrick, *THIS JOURNAL*, **42**, 946 (1920).

(19) Palmer and Clark, *Proc. Roy. Soc. (London)*, **A149**, 360 (1935).

the slopes of the plots of equation (E). If we disregard the butane run for the moment, the  $v_m$  values calculated from the isotherms are consistent with each other, giving a mean surface of 708 square meters per gram of charcoal if we use

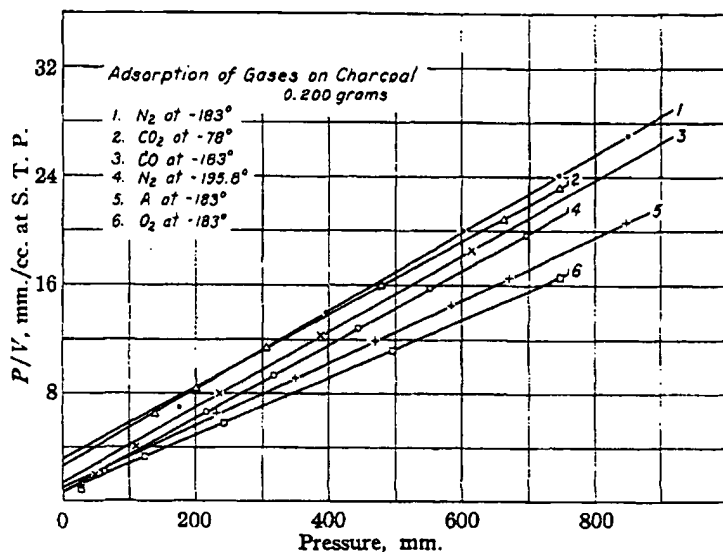


Fig. 5.

molecular cross-sectional areas calculated from the solid state, and 829 square meters per gram if the molecular areas are calculated from the liquefied gases. The maximum deviation of surface areas from the mean for the seven isotherms is about 9% on the basis of solid packing, and 8% on the basis of liquid packing. Butane adsorption on charcoal is decidedly smaller (about 25%) than one would expect on the basis of the estimated cross-sectional area of the butane molecule. It seems probable that some of the capillaries are so small in diameter that molecules as large as butane cannot enter them. Similar phenomena were noted by other investigators before; a discussion of these, under the name "persorption," is given by McBain.<sup>21</sup>

Equation (E), as mentioned before, is of the form of Langmuir's equation, with the usual constant  $k$  replaced by  $c/p_0$ . Since the temperature dependence of  $p_0$ ,  $c$ , and  $v_m$  is known, or can be evaluated, equation (E) can be used to calculate an isotherm at one temperature from that at another. As an illus-

tration, the curves in Fig. 6 for the data of Goldman and Polanyi<sup>22</sup> on the adsorption of ethyl chloride by charcoal are shown. From the 0° isotherm plotted according to equation (E) values of  $v_m$  and  $c$  were obtained. Assuming that  $v_m$  is the same at -15 and 20° as at 0° (since the temperature range is rather narrow), and that  $c$ , as before, can be represented by the exponential  $e^{E_1 - E_L/RT}$ , we have calculated the isotherms for -15.3 and 20°. The calculated values are represented by the curves, the points are experimental. Here, as in previous instances, equation (E) appears applicable only to that portion of the isotherm which corresponds to  $p/p_0$  values greater than 0.1. In the higher pressure region, however ( $p/p_0$  being between 0.1 and 0.95), the calculated isotherms agree quite well with the observed points.

For more extended calculation of the temperature dependence of these Langmuir-type isotherms it would be

necessary to make assumptions in regard to the temperature dependence of  $v_m$  or to determine  $v_m$  over a sufficiently wide temperature range to be able to estimate it for other temperatures. For

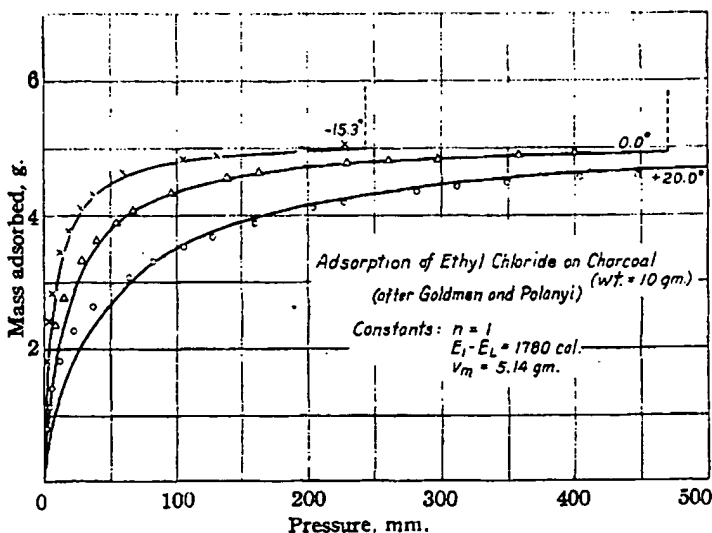


Fig. 6.

some substances, furthermore,  $E_1 - E_L$  will vary considerably with temperature and cause calculated isotherms to deviate more or less seriously from the experimental points. With these limita-

(21) McBain, "The Sorption of Gases by Solids," George Routledge and Sons, Ltd., London, 1932, p. 169.

(22) Goldman and Polanyi, *Z. physik. Chem.*, **132**, 321 (1928).

tions it seems that equation (E) ought to be useful for calculating Langmuir isotherms of van der Waals adsorption at one temperature from those at another.

TABLE V

VALUES OF  $v_m$  FOR ADSORPTION ISOTHERMS ON CHARCOAL

Gas	Temp., °C.	Curve in Fig. 5	$v_m$ , cc./g.	Surface in Solid packing	sq. m./g. Liquid packing
N <sub>2</sub>	-195.8	4	181.5	677	795
N <sub>2</sub>	-183	1	173.0	646	795
A	-195.8		215.5	746	804
A	-183	5	215.5	746	839
O <sub>2</sub>	-183	6	234.6	787	894
CO	-183	3	179.5	665	820
CO <sub>2</sub>	-78	2	185.5	707	853
C <sub>4</sub> H <sub>10</sub>	0		63.0	545	546

### Summary

1. A critical discussion of the polarization theory of multimolecular adsorption is presented. It is shown that the adsorption energy due to attraction of dipoles induced into a non-polar gas like argon is insufficient to constitute a major portion of the binding energy between adsorbed layers.

2. Derivation of adsorption isotherm equations for multimolecular adsorption are carried out on the assumption that the same forces that produce condensation are also responsible for multimolecular adsorption.

3. Numerous applications of the equations are given to experimental adsorption isotherms obtained by other investigators as well as by us.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY AND THE COLLEGE OF THE CITY OF NEW YORK]

## The Synthesis of 1,4-Dimethylphenanthrene by Cyclodehydration Methods

BY DOMENICK PAPA, DAVID PERLMAN AND MARSTON T. BOGERT

In a recent article, Akin, Stamatoff, and Bogert<sup>1</sup> reported the synthesis of 1,4-dimethylphenanthrene from *p*-xylene by the familiar Pschorr reaction, in which they obtained a product quite different from that secured from the same initial material by Bardhan and Sengupta,<sup>2</sup> by another series of reactions, and to which the latter investigators assigned the same constitution.

The experimental results published by Akin, Stamatoff, and Bogert indicated, however, that the Bardhan and Sengupta hydrocarbon was probably the 1,3-dimethyl isomer, previously prepared by Bogert and Stamatoff,<sup>3</sup> and by Haworth, Mavin, and Sheldrick.<sup>4</sup>

At the time, it was suggested by Akin, Stamatoff, and Bogert, although they could not rearrange their own product to the 1,3-dimethyl isomer by selenium fusion, that perhaps something of this kind had happened in the final step of the Bardhan and Sengupta synthesis. We have therefore synthesized the 1,4-dimethylphenanthrene by two slightly different methods, from *p*-xylylethyl cyclohexanols, dehydrogenating the resulting octahydro compounds by either sulfur or selenium,

as the final step, and in both cases obtained a dimethylphenanthrene whose properties agreed with the 1,4- compound of Akin, Stamatoff, and Bogert, and without any evidence of the migration of one of the *p*-xylene methyl groups under the conditions of our experiments. Our suggested explanation of Bardhan and Sengupta's results, therefore, is not supported by this evidence.

These two syntheses were as shown in the chart.

### Experimental

**beta-(*p*-Xylyl)-ethanol**, was prepared from bromo-*p*-xylene and ethylene oxide by the Grignard reaction, following the method described by Dreger<sup>5</sup> for the synthesis of *n*-hexyl alcohol, in a yield of 61% and a boiling point of 108–111° at 4 mm. On a redistilled sample, the physical constants were: b. p. 105–106° at 3 mm.,  $d_{25}^{25}$ , 0.9946,  $n_D^{25}$  1.5286,  $M_D$  calcd. 46.30,  $M_D$  obsd. 46.48. Bardhan and Sengupta, who synthesized it in a different way, gave the b. p. as 110–113° at 5 mm.

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O: C, 79.94; H, 9.39. Found: C, 79.64; H, 9.40.

**Phenylurethan**.—Small white rosetts of thin needles from petroleum ether, m. p. 79–79.5° (corr.).

*Anal.* Calcd. for C<sub>17</sub>H<sub>15</sub>O<sub>2</sub>N: N, 5.20. Found: N, 5.29.

**beta-(*p*-Xylyl)-ethyl bromide (I)** was obtained from the above alcohol and hydrobromic acid, according to the

(1) Akin, Stamatoff and Bogert, *THIS JOURNAL*, **59**, 1268 (1937).

(2) Bardhan and Sengupta, *J. Chem. Soc.*, 2520 (1932).

(3) Bogert and Stamatoff, *Rec. trav. chim.*, **52**, 583 (1933).

(4) Haworth, Mavin, and Sheldrick, *J. Chem. Soc.*, 454 (1934).

(5) Dreger, "Organic Syntheses," Coll. Vol. I, 1932, p. 299.